

Kenyatta University, Chemistry
Department

SCH 200: Atomic Structure and Chemical Bonding

Lecture Notes

UNIT 2

Introduction to Quantum Mechanics

Objectives

At the end of this unit understand:

1. The de Broglie relationship and wave particle duality.
2. The importance of the Heisenberg's uncertainty principle.
3. That the Schrodinger equation can be solved exactly for the hydrogen atom
4. What is meant by atomic orbital
5. The quantum rules for describing atomic orbitals
6. The spatial orientations of s, p, d, and f atomic orbitals.

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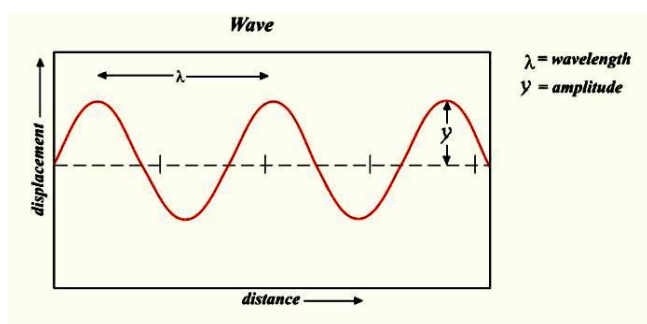
2.0 The Quantum Model of an Atom

Our current understanding of the electronic structure of an atom is based on quantum mechanics. A fundamental concept of quantum mechanics is that all matter has wave and particle-like properties. In this section we shall discuss the wave-particle duality of matter and the Schrodinger wave equation and its solutions for the hydrogen atom.

2.1 The Wave-Particle Duality of matter

First a review of Waves

A wave is a disturbance that travels through space and time, usually accompanied by the transfer of energy. They are characterized by wavelengths and amplitude. Each wave is characterized by a wavelength, λ , an amplitude, A and a frequency, ν .



The energy of a wave is related to its wavelength by the equation $E = hc/\lambda$, where c is the speed of light and λ is the wavelength of the wave.

The de Broglie Hypothesis

Albert Einstein explained the photoelectric effect by proposing that radiation consists of a stream of particles now known as photons. Following these observations Louis Victor de Broglie (1924) De Broglie, in his research, decided to look at Einstein's research on photons – or particles of light – and how it was possible for light to be considered both a wave and a particle. He postulated that the dual nature of the light must be “expanded” to *ALL* matter. In other words, all material particles possess wave-like properties, characterized by the wavelength, λ_B , related to the momentum p of the particle in the same way as for light.

$\lambda = \frac{h}{p}$, where p is the momentum, h is Planck's constant and λ_B is de Broglie wavelength of the particle wave.

This can be arrived at from Einstein's special relativity theory and Planck's quantization theory. According to Einstein's theory, the fundamental law relating energy E , and the mass m of a particle is

$$E = mc^2$$

From Plank's quantum theory, $E = h\nu$. Therefore, $E = h\nu = mc^2$. But $\nu = \frac{c}{\lambda}$

$$\lambda = \frac{h}{mc}$$

This equation is immediately applicable to photons but not atomic particles which cannot have a velocity equal to the speed of light. Thus de Broglie modified this equation by replacing the speed of light c with the velocity of the atomic particle v . Thus,

$$\lambda = \frac{h}{mv},$$

λ = wavelength of the moving particle

h = Planck's constant = 6.626×10^{-34} J.s

m = mass of the moving particle.

and since $mv = p$, the momentum of the particle, then $\lambda = \frac{h}{p}$

That is, all particles in motion have a wavelength that depends on the particle's momentum. The larger the momentum, the smaller the wavelength. For this contribution De Broglie received the Nobel Prize in Physics in 1929.

De Broglie's equation was confirmed experimentally three years later. In 1927, Davisson and Germer at Bell Laboratories showed that when a beam of electrons was directed at a nickel crystal, a diffraction pattern was observed. The pattern obtained was similar to that obtained when light is allowed through a thin slit and allowed to fall on a screen. Thus electrons could be diffracted just like light waves and so they too possessed wave properties. For this work they received the Nobel Prize in Physics in 1932. This was the beginning of wave mechanics.

The wave-particle duality strikes at the heart of classical physics where particles and waves are treated as entirely distinct entities. Clearly a new type of mechanics had to be devised – *Quantum Mechanics*.

De Broglie's research on the wave-particle duality is one of the biggest paradigms in quantum mechanics, and even physics itself. In 1929 Louis, 7th duc de Broglie received the Nobel Prize in Physics for his "discovery of the wave nature of electrons." It was a very special moment in history, and for Louis de Broglie himself.

He died in 1987, in Paris, France, having never been married. Let us pay him tribute as CW Oseen, the Chairman for the Nobel Committee for Physics, did when he said about de Broglie:

"You have covered in fresh glory a name already crowned for centuries with honour."

2.2 Heisenberg Uncertainty Principle

The dual nature of matter, both particles and wavelike properties, raised questions regarding the applicability of the classical physics to the motion of small bodies the size of atoms and subatomic particles like electrons. It was known that a wave extends in space and its location is not precisely defined. Thus if electrons can have wave as well as particulate properties under appropriate conditions then their motion cannot be considered only under the classical mechanics laws.

From the foregoing considerations the German Physicist Werner Heisenberg (1901-1961) concluded that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of any object. The uncertainty principle states that *it is impossible to simultaneously know both the position and momentum of an object as small as an electron*. Mathematically it can be stated as follow:

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

Δx = error (or uncertainty) in position

Δp = error (or uncertainty) in momentum

The principle implies that the more accurately we know the position of the electron, the less accurately we know the momentum and vice versa.

Consequences of the Heisenberg Uncertainty Principle

- 1 It did away with Bohr's ideas of electrons being in definite orbits where the position and velocity are known exactly. These were replaced by the probability of finding an electron in a particular position or volume of space. Thus orbits were replaced with orbitals and electron particle replaced with electron cloud. Thus an orbital is a volume in space where 99% of the electron cloud is expected to be found.
- 2 It demonstrated the need to find a microscopic/atomic equation equivalent to the Newton's second law of motion which would have to include the Planck postulate $E = h\nu$ as well as the de Broglie wave postulate.

2.3 The Schrödinger Wave Equation



After the confirmation that electrons too could possess wave properties, it was time to find a wave equation that would describe the motion of the electron in an atom. It is one of the postulates of quantum mechanics that for a physical system consisting of a particle there is an associated wave function. This wave function determines everything that can be known about the system.

Erwin Schrodinger (1887 – 1961) proposed the mathematical formulation of the electron as a wave in 1926. This is now known as the quantum mechanical model of the atom. Schrodinger's equation for the electron involves complex mathematics which is out of the scope of this course. We shall only use its results and interpretations.

In its simplest form the time-independent Schrödinger equation is written;

$$H\psi = E\psi$$

where H = the Hamiltonian operator¹

ψ = is the wave function (the solutions describing the possible electron waves)

E = the energy associated with the wave

The Hamiltonian operator involves derivatives that operate on the wave function. The equation implies that if the operations represented by the Hamiltonian, H, are performed on the function ψ , the result will be a constant (energy) multiplied by the wave function, ψ .

The other way of presenting the Schrödinger equation is

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

where E = total energy of the particle

V = potential energy of the particle

m = mass of the particle/electron

$$\nabla^2 \text{ (del squared also called Laplacian operator)} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

E - V = kinetic energy of the particle

ψ = is the wave function.

Thus, the equation in full is;

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

This is the celebrated time independent Schrodinger equation. It describes the wave properties of an electron in terms of its position, mass, total energy, and potential energy.

It is applicable only in the case where the state of the system does not change with time. For example in atoms electrons remain in a given energy level (called orbit by Bohr) except when excited. This suggests that the motion of the electron in an atom is analogous to a system of standing waves. Some common examples of standing waves are: a string fixed at both ends plucked to produce a musical tone in a guitar or violin.

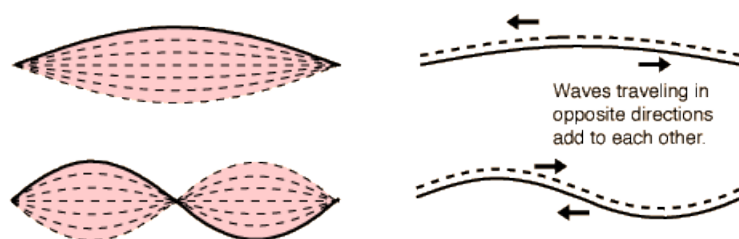


Figure 2.1 The fundamental and second harmonic standing waves for a stretched string.(source: <http://hyperphysics.phy-astr.gsu.edu/hbase/waves/standw.html>)

The term **standing wave** is often applied to a resonant mode of an extended vibrating object. The resonance is created by constructive interference of two waves which travel in opposite

¹ An operator is an instruction or set of instructions that states what to do with the function that follows it. It may be a simple instruction like “multiply the following function with 6,” or it may be much more complicated than the Hamiltonian.

directions in the medium, but the visual effect is that of an entire system moving in simple harmonic motion.

The main task of applying the Schrodinger equation to a given problem is two-fold

- to obtain a suitable expression of ψ showing how the wave amplitude varies with distance along the x, y and z axes and then derive the solutions to the differential equation.
- To determine the energy associated with each solution ψ .

Acceptable solutions (wave functions) are called *Eigen² functions* and the energies associated with the acceptable *Eigen functions* are called *Eigen values*.

2.4 Solutions to the Schrodinger Equation

The Schrodinger equation being a differential equation of the second order has innumerable many solutions but not all of these can be accepted as physically meaningful solutions. An acceptable solution must meet the following conditions:

- ψ must be a solution of the Schrodinger equation.
- ψ must be finite and single valued for all values of the coordinates
- ψ must be continuous functions of the coordinates
- $\frac{\partial \psi}{\partial x}$, $\frac{\partial \psi}{\partial y}$ and $\frac{\partial \psi}{\partial z}$ must be continuous functions of x, y, and z respectively
- The probability of finding the electron over all space from $+\infty$ to $-\infty$ must be equal to one. The probability of finding the electron at any point in space is given by the square of the wave function i.e. ψ^2 . Thus the sum of all probabilities

$$\int_{-\infty}^{\infty} \psi^2 dx dy dz = 1$$

Notes

1. ψ has positive and negative amplitudes, like any wave.
2. Due to the wave-like behavior of an electron, we cannot pin down its position and momentum at the same time (Heisenberg Uncertainty Principle). In other words, we do not know the exact location of an electron and how it moves from one spot to another in an atom.
3. ψ has no physical significance but depends on x, y and z coordinates. Each ψ describes the wave properties of a given electron in a particular orbital. Every ψ matches an atomic orbital but it is not an atomic orbital.
4. ψ^2 at any point around the nucleus is measure of the electronic charge density at that point. It may therefore be regarded as the probability density function for finding the electron at that point in space. the value of $\psi^2 d\tau$ represents the probability of finding the electron in the volume element $d\tau$ ($d\tau = dx.dy.dz$).
5. Types of functions (ψ) usually chosen include the

² Eigenvalue" comes from the German "Eigenwert" which means proper or characteristic value. "Eigenfunction" is from "Eigenfunktion" meaning "proper or characteristic function".

- Exponential functions; $\psi = \exp x$
- Sine functions; $\psi = \sin x$ and
- Cosine functions; $\psi = \cos x$

These are chosen because their second derivatives give the same function multiplied by a constant i.e.

$$\frac{\partial^2 \psi}{\partial x^2} = k \frac{\partial^2 \psi}{\partial x^2}$$

2.4.1 Solution of the Schrodinger Equations for some simple systems

The mathematics entailed in the complete solution of the wave equation even for the simplest atomic systems, namely, the hydrogen and hydrogen-like atoms, is complicated. Nevertheless, even a relatively limited mathematical background is sufficient for one to grasp the basic procedures involved in the wave mechanical treatment. To this end, we consider here a very simple problem, namely, the particle-in-a box problem, which, though hypothetical, bears some relevance to real molecular problems.

Broadly, our objectives in considering this problem are:

- To illustrate quantum mechanical principles
- To illustrate how Schrödinger equation is solved satisfying the given boundary conditions
- To show how discrete energy levels arise when a small particle is confined to a region of space.
- To illustrate how Schrödinger equation can predict the absorption spectrum of some linear conjugated molecules by treating the π electrons as free particles in a 1-dimensional box with infinite walls.

2.4.2 The particle in a one-dimensional box

Consider a particle of mass m , bouncing back and forth between the walls of a box. Suppose that the particle travels only along the x-axis and is confined only to the area between $x = 0$ and $x = a$ by two infinitely hard walls so that the particle has no chance of penetrating them. Suppose that the particle does not lose energy when it collides with such walls, so that its total energy remains constant. The Schrödinger equation for the motion of a particle in one dimension is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} [E - V(x)] \psi(x) = 0$$

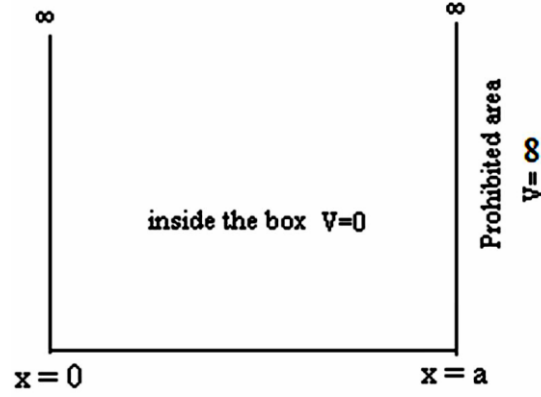


Figure 2: One-dimensional potential box particle box walls of infinite height at $x = 0$ and $x = a$

Since the potential outside the box is infinitely high, the probability of finding the particle outside must be zero, that is to say, ψ^2 and hence ψ must be zero when $0 > x > a$. To avoid a discontinuity at $x = 0$ and $x = a$, the wave function must be zero at these points also and so the boundary conditions to be satisfied in the present problems are $\psi = 0$ at $x = 0$ and $\psi = 0$ at $x = a$. Our task is now to find what is inside the box, in the region $0 < x < a$.

Since $V = 0$ inside the box, the one –dimensional wave equation reduces to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E \psi(x) = 0 \text{ or } \frac{\partial^2 \psi}{\partial x^2} = -\frac{8\pi^2 m}{h^2} E \psi$$

Since E is positive, the coefficient of ψ is a negative constant at any value of E , and the differential equation can be written

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 E \psi \quad \text{Where } k^2 = -\frac{8\pi^2 m}{h^2} E$$

The solution to this well-known general equation is

$$\psi = A \sin kx + B \cos kx$$

where the constants A , B and k remain to be determined.

The complete wave function may be written as follows:

$$\psi = A \sin \left(\frac{8\pi^2 m}{h^2} E \right)^{1/2} x + B \cos \left(\frac{8\pi^2 m}{h^2} E \right)^{1/2} x$$

Where A and B are integration constants.

Applying the condition $\psi = 0$ at $x = 0$

For $x = 0$, $\sin kx = 0$ but $\cos kx = 1$, and so $\psi = B$ at $x = 0$. However, boundary conditions require that ψ must be zero at $x = 0$. This is only possible in this case if $B = 0$. Consequently, the wave function reduces to

$$\psi = A \sin kx \text{ or } \psi = A \sin \left(\frac{8\pi^2 m}{h^2} E \right)^{1/2} x$$

Applying the condition $\psi = 0$ at $x = a$

Since $x = a$ it follows that, $\psi = A \sin ka = 0$

Since $A \neq 0$, then $A \sin ka = 0$, only if ka is an integral multiple of π , i.e. $ka = n\pi$. Therefore replacing k with $n\pi/a$ in the wave function leads to

$$\psi = A \sin \frac{n\pi}{a} x$$

This implies then that $\left(\frac{8\pi^2 m}{h^2} E \right)^{1/2} = \frac{n\pi}{a}$, where $n = 1, 2, 3, \dots$

Upon rearrangement and making E the subject of this equation we obtain $E = \frac{n^2 h^2}{8ma^2}$, where $n = 1, 2, 3, \dots$

n cannot be zero, since this would make ψ^2 zero between $x = 0$ and $x = a$ i.e. the particle would not be in the box. Thus in general the energy of the particle in the one-dimensional well is given by $E_n = \frac{n^2 h^2}{8ma^2}$

Where $n = 1, 2, 3$ and is the quantum number determining the energy of a particle of mass m confined within a well of length a .

So we see that the limitations placed on the value of ψ lead to quantized energy levels whose spacing is determined by m and a . The corresponding wave function is given by

$$\psi_n = A \sin \frac{n\pi}{a} x$$

Therefore, only certain values of E , namely, E_n , are possible, and these are the only ones allowed. The energy values E_n are usually called *eigen values* and ψ_n *eigen functions*; the integer n may be termed a *quantum number*, and it arises here merely as a consequence of the boundary conditions imposed. This quantum number can be equal to 1, 2, 3....but not zero because ψ , and hence ψ^2 or probability of finding the particle, would be zero everywhere within the box.

Example

Calculate the permitted energies of an electron confined in a box 1 \AA wide.

Solution

The permitted energies are given by

$$E_n = \frac{n^2 h^2}{8ma^2}; \quad 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$\begin{aligned} E_n &= \frac{n^2 (6.623 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} (1 \times 10^{-10})^2} \\ &= 6.038 \times 10^{-18} n^2 \text{ J} \\ &= 37.69 n^2 \text{ eV} \\ &\approx 38 n^2 \text{ eV} \end{aligned}$$

The minimum energy that said electron can have is 38 eV, corresponding to $n = 1$. The other permitted energy levels are:

$$\begin{aligned} E_2 &= (2)^2 \times 38 = 152 \text{ eV} \\ E_3 &= (3)^2 \times 38 = 342 \text{ eV} \\ E_4 &= (4)^2 \times 38 = 608 \text{ eV, etc} \end{aligned}$$

Since n in $E_n = \frac{n^2 h^2}{8ma^2}$ cannot be zero, the minimum energy of E_1 corresponds to $n = 1$. It is the zero point energy (ZPE) of the system. This implies that matter cannot exist without motion.

The value of A is determined from the normalization condition. This involves setting to unity the integral of the probability between two fixed limits. Thus, since the particle must be somewhere between $x = 0$ and $x = a$, the integral of the probability between these two limits must, obviously, be unity, that is

$$\int_0^a P_x dx = \int_0^a \psi_n^2 dx = 1$$

Substituting $\psi_n = A \sin \frac{n\pi}{a} x$

$$\begin{aligned} \int_0^a \left(A \sin \frac{n\pi}{a} x \right)^2 dx &= 1 \\ A^2 \int_0^a \frac{1}{2} \left[1 - \cos \frac{2n\pi}{a} x \right] dx &= 1 \\ \frac{1}{2} A^2 \left[x - \frac{a}{2n\pi} \sin \frac{2n\pi}{a} x \right]_0^a &= 1 \end{aligned}$$

$$\text{Hence } A = \sqrt{\frac{2}{a}}$$

Therefore, the normalized wave function is given by $\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x$. The plots of ψ and ψ^2 for a particle in a 1-dimensional box appear as follows:

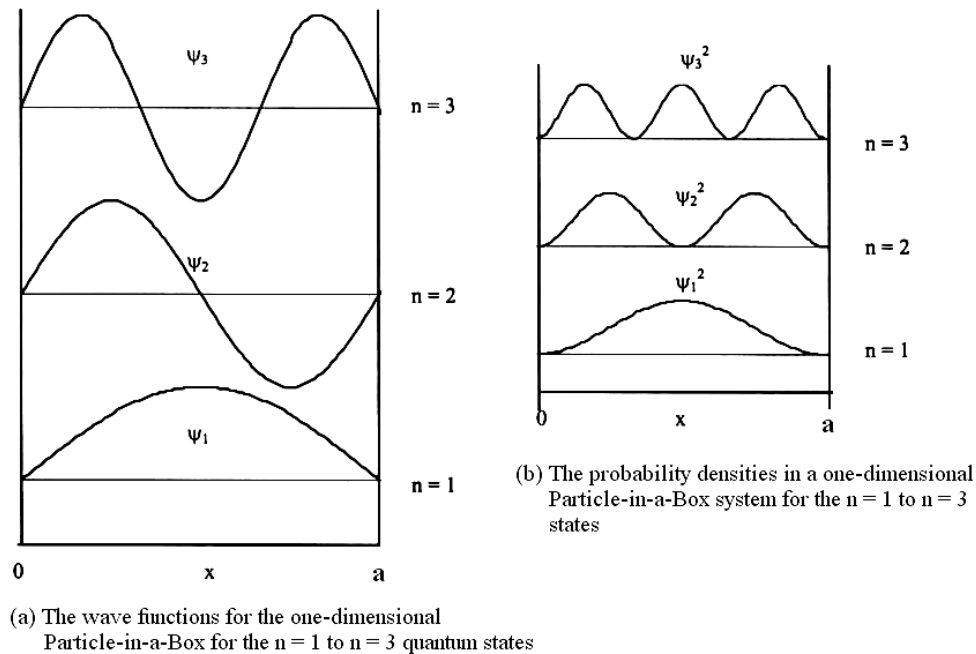


Figure 3: Variation of ψ and ψ^2 with x for $n = 1, 2$, and 3 for a particle in one-dimensional box

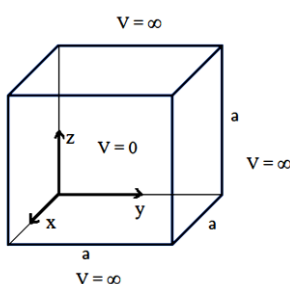
Notes

- As n increases E increases and ψ becomes more wiggly. The λ becomes shorter and shorter.
- The probability finding the particle at the various points of the well along the allowed length l (or a) is not the same. For values of $n > 1$, ψ^2 at certain points = 0 which is classically impossible.

Study questions

- What happens if the walls are removed?
- What happens if finite walls are used?
 - Case 1: $E < V_0$
 - Case 1: $E > V_0$
- Plot the function $\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x$ if $n = 6$, $a = 1$, i.e. $0 \leq x \leq 1$ and $\pi = 180^\circ$

2.4.3 The particle in a three dimensional box



Particles normally are capable of travelling in three-dimensions, and the particle in a one-dimensional box can readily be expanded into three dimensions. In place of one dimensional box, we now consider a three dimensional square box having sides a_x , a_y and a_z , and with potential zero everywhere inside the box but infinite outside. The Hamiltonian for the particle will correspond to kinetic energy in the x , y , and z coordinates. The wave function $\psi(x, y, z)$ in this case depends on three coordinates x , y and z . The Schrödinger equation for such a

particle is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E \psi = 0$$

The motion of the particle is independent in each dimension making this problem separable. Because the problem is separable, the Hamiltonian can be written as a sum of the Hamiltonians for each dimension.

$$H(x, y, z) = H(x) + H(y) + H(z)$$

In order to satisfy the Schrodinger equation the wave function must be the **product** of wave functions in each coordinate.

$$\psi(x, y, z) = \psi(x) \cdot \psi(y) \cdot \psi(z)$$

The system in each dimension is identical to a Particle-in-a-one-dimensional- Box. As a result, Equation above is a product of the wave functions for the one-dimensional Particle-in-a-Box. The solution of this equation leads to

$$\psi(x, y, z) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} x \cdot \sqrt{\frac{2}{a}} \sin \frac{n_y \pi}{a} y \cdot \sqrt{\frac{2}{a}} \sin \frac{n_z \pi}{a} z,$$

and the energy eigenvalues are found by applying the equation above to the Hamiltonian given earlier. The energy eigenvalues will depend on three different quantum numbers: n_x , n_y , and n_z corresponding to each coordinate. Thus, $E_n = E_x + E_y + E_z$, or

$$E_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2), \text{ where } n_x = 1, 2, 3, \dots; n_y = 1, 2, 3, \dots; n_z = 1, 2, 3, \dots;$$

The energy thus depends on the sum of the squares of the three quantum numbers (n_x , n_y , and n_z) and evidently, it is possible for groups of different states, each specified by unique set of the three quantum numbers, to possess the *same energy*. In such a case, the energy level and the corresponding independent states are said to be *degenerate*. The zero point energy is

$$E_{(1,1,1)} = \frac{3h^2}{8ma^2}, \text{ corresponding to the wave function } \psi_{(1,1,1)}.$$

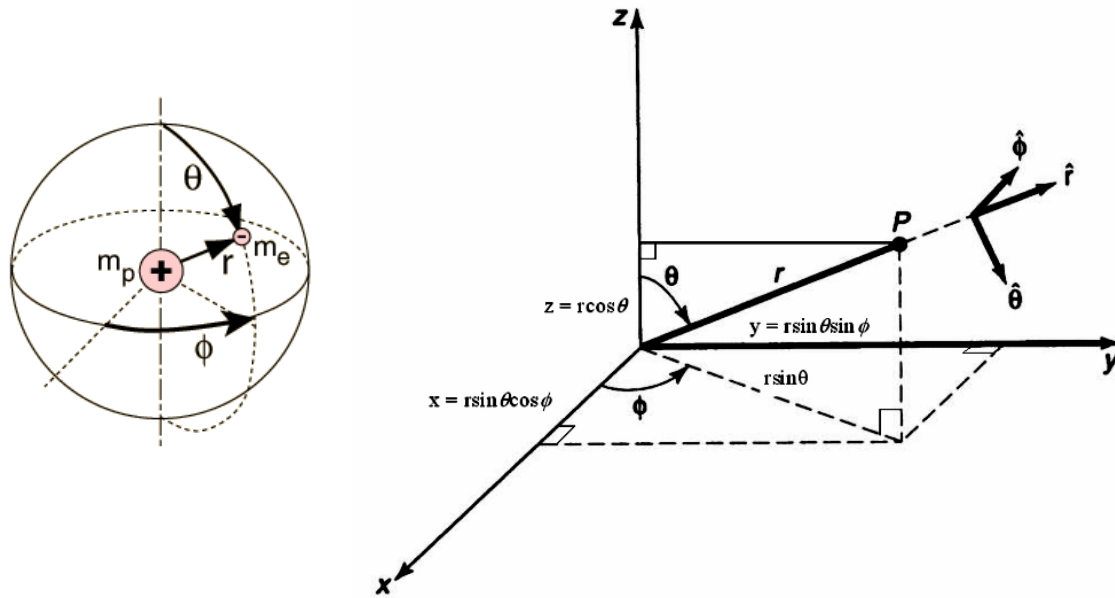
The degeneracy breaks down on applying even a small modification to the system. This has relevance to what is often observed in practice, such as the splitting of spectral lines in a magnetic or electric field. As a result of the application of a magnetic or electric field the degenerate levels break up into separate levels, and consequently, spectral lines which were single become multiplets.

2.4.4 The hydrogen atom and hydrogen-like atoms

Hydrogen has the simplest atomic structure. It consists of only one electron moving under the influence of the field of force of the nucleus. In a way this is similar to considering a particle of mass m free to rotate on the surface of a sphere with a constant radius r .

The wave function depends on the coordinates of the electron, and since the atom has spherical symmetry it is better to use the spherical coordinates r, θ, ϕ rather than Cartesian coordinates. A point in space denoted by the Cartesian coordinates (x, y, z) will now be denoted by the polar coordinates (r, θ, ϕ) . Thus, the electron moves on the surface of a sphere

whose centre coincides with the nucleus of the atom. Cartesian and polar coordinates are related as follows:



$$-\infty < x, y, z < \infty; 0 < r < \infty; 0 < \theta < 180 \text{ and } 0 < \phi < 360$$

The electron in the hydrogen atom sees a spherically symmetric potential, so it is logical to use spherical polar coordinates to develop the Schrodinger equation. The potential energy of the electron with charge $-e$ in the vicinity of a proton of charge e is given by the Coulomb expression

$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

In polar coordinates the Schrodinger equation takes the form

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} [E - V(r, \theta, \phi)] \psi = 0$$

Since this equation is a sum of partial derivatives with respect to r , θ , and ϕ it is separable (i.e. it can be solved by the method of separation of variables). As a result, the wave function $\psi(r, \theta, \phi)$ will be a product of wave functions written in terms of the separate variables r, θ , and ϕ .

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

where $R(r)$ is the radial component, and the product $\Theta(\theta)\Phi(\phi)$ is the angular component of the wave function, and is denoted $Y(\theta, \phi)$. $\Theta(\theta)$ is known as the colatitude equation while $\Phi(\phi)$ is known as the Azimuthal equation.

Notes

- The radial function $R(r)$ describes how ψ of the electron varies with the radial distance from the nucleus while θ and ϕ are kept constant. It determines the spatial extent of the orbital (i.e. how large or small an orbital is).
- $\Theta(\theta)$ describes how ψ varies with the zenith angle θ along a constant meridian on a sphere centred at the nucleus while r and ϕ are kept constant.

- c) $\Phi(\phi)$ describes how ψ varies with the azimuthal angle ϕ along a constant meridian on a sphere centred at the nucleus while r and θ are kept constant.

The product $\Theta(\theta) \Phi(\phi)$ is known as the angular wave function and is sometimes denoted $Y(\theta, \phi)$. It describes the shape of an atomic orbital and its orientation in space. Thus $\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r) Y(\theta, \phi)$.

Quantum numbers

Solution of the Schrodinger equation for hydrogen involves solving these three functions separately. When this is done, while imposing boundary conditions that ensure that the Born interpretation³ is tenable, three quantum numbers, n , l and m_l arise. Thus, the wave functions are labeled ψ_{nlm_l} . The energies might be expected to depend on all three quantum numbers, or at least the first two, but the hydrogen atom is peculiar in that the energy depends only on n . Thus it is called the *principal quantum number*. l is known as the *angular or orbital quantum number* while m_l is known as the *magnetic quantum number*. They arise from the freedom of the electron to move in three dimensions while n arises from the freedom of the electron to vary its distance from the nucleus⁴.

The quantum numbers n , l and m_l obey the following quantum rules:

- i) *Principal quantum number* takes only integral values, i.e. $n = 1, 2, 3, \dots, \infty$. It determines the major part of the energy associated with a given wave function. Therefore all the solutions having the same values of n but different values of l and m will be energetically degenerate. For example, the lowest energy wave function $n = 1$ and $l = 0$ and $m = 0$. Since for this function no other choices are available this level is said to be non-degenerate.
- ii) *Orbital angular momentum quantum number* takes integral values including zero i.e. $l = 0, 1, 2, \dots, (n - 1)$. It describes the orbital angular momentum of the electron. It determines the shape of the orbital.
- iii) *Magnetic quantum number* takes depending on the value of l . Thus $m_l = +l, +l-1, \dots, 0, \dots, -(l-1), -l$. It is related to the behaviour of electronic energy levels when subjected to an external magnetic field i.e. It determines the orientation of the angular momentum vector in a magnetic field. When no field is present, all m_l values (all three p orbitals or all d orbitals) have the same energy. Generally it determines the spatial orientation of an atomic orbital.

Each solutions to Schrodinger equation, ψ , is characterized by the values of the three quantum numbers and every allowed set of values of the quantum numbers together with the associated wave function describes an atomic orbital.

The values of l and m_l are dependent upon the value of n , and so it can be concluded that the value of n is concerned with a particular set of atomic orbitals all characterized by the given value of n . For any given value of n (except $n = 1$) there is more than one permitted value of l . The notation that is used to distinguish orbitals with different l values consists of a code

³ The Born interpretation of ψ is that the product $\psi^*(x) \cdot \psi(x) dx$ is proportional to the probability of finding the particle in an infinitesimal region between x and $x+dx$.

⁴ A detailed discussion of the way these quantum numbers arise can be obtained from the chemistry links here: <http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>

letters associated with each value. The letters were used by 19th century spectroscopists to describe aspects of line spectra. In terms of the quantum number designations of electron states, the notation is as follows:

Table 1

Spectroscopic meaning of letter	n =1	n =2	n =3	n =4
s -sharp	$l = 0$ 1s	2s	3s	4s
p - principal	$l = 1$	2p	3p	4p
d -diffuse	$l = 2$		3d	4d
f - fundamental	$l = 3$			4f
g	$l = 4$	<i>Beyond this point, the notation just follows the alphabet</i>		
h	$l = 5$			

The numerical value of n and the code letter of the value of l are sufficient for a general description of an atomic orbital. For example in the level $n = 1$, $l = 0$ and we have one atomic orbital labeled 1s. In the level $n = 2$, $l = 1, 0$ and we have 2p and 2s orbitals. The importance of m_l is to determine the number of orbitals of the same l value that are oriented differently spatially. For example, if $l = 2$, then there are five $(2l+1)$ possible m_l values, $m_l = 2, 1, 0, -1, -2$ and hence five differently spatially orientated orbitals characterized by $l = 2$. Thus, from these three quantum numbers, the orbitals at each level characterized by n can be determined.

For the hydrogen atom, all the orbitals having a particular value of n have the same energy (i.e. they are degenerate).

Self-assessment Questions

- If the value of n is 5, what are the permitted values of l ?
- If the value of $l = 3$, what are the permitted values of m_l ?
- Which atomic orbitals are represented by the following quantum number values?
 - $n = 4, l = 3, m_l = -2$
 - $n = 2, l = 0, m_l = 0$
 - $n = 5, l = 2, m_l = 2$

2.4.5 Shapes and spatial orientations of hydrogen atomic orbitals

The wave functions of the hydrogen atom are important because they determine the distribution of the electron in space. We mentioned earlier that the solutions to the Schrodinger equation for the hydrogen atom may be represented by the equation:

$$\psi_{n,l,m_l} = R_{n,l}(r) Y_{l,m_l}(\theta, \phi), \text{ where,}$$

R(r) is the radial function and
Y(θ, ϕ) is the angular function

The radial and angular wave functions for values of the principal quantum numbers $n = 1, 2$ and 3, respectively are given in the Table 3. The term a_0 is the Bohr radius with a value of 0.529 Å.

Table 2: Hydrogen Wave function and their components

Wave functions and their components					
n	ℓ	m	R_{nl}	Y_{lm}	$\psi_{nlm} = R_{nl} Y_{lm}$
1	0	0	$2 \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\left(\frac{1}{2a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta$	$\frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}} \frac{r}{a_0} e^{-r/2a_0}$	$\pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$	$\frac{1}{8\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$2 \left(\frac{1}{3a_0}\right)^{3/2} \left(1 - \frac{2}{3} \frac{r}{a_0} + \frac{2}{27} \left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$	$\frac{1}{2\sqrt{\pi}}$	$\frac{1}{81\sqrt{3\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(27 - 18 \frac{r}{a_0} + 2 \left(\frac{r}{a_0}\right)^2\right) e^{-r/3a_0}$
3	1	0	$\left(\frac{1}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \left(1 - \frac{1}{6} \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta$	$\frac{1}{81\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\left(\frac{1}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \left(1 - \frac{1}{6} \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{\pm i\phi}$	$\frac{1}{81\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	± 2	$\left(\frac{1}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$	$\frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{\pm 2i\phi}$	$\frac{1}{162\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

Notes

1. The form of the angular function depends upon the value of the magnetic quantum number, m_l , in addition to the value of l ; when the value of l is greater than zero the angular functions contain the term i which is the same as -1 .
2. Functions containing the term i are imaginary or complex functions. These are not useful to chemists. Chemists prefer to use real functions i.e. those that do not contain i . To obtain real function from complex functions, it is necessary to take linear combinations of the complex angular functions so that the resulting functions are real and can be visualized.

Example

The 2p orbitals for which the values of m_l are 1 and -1 respectively are combined in two linear combinations so that the orbitals do not have imaginary parts and can be visualised diagrammatically. $2p(m_l = 1) + 2p(m_l = -1)$ combination leads to $2p_x$ orbital while $2p(m_l = 1) - 2p(m_l = -1)$ combination leads to the $2p_y$ orbital. The same can be done for 3p orbitals as well as 3d orbitals with non-zero m_l values.

3. The exponential terms containing i may be converted to trigonometric terms by using Euler's identities: $e^{i\phi} = \cos\phi + i\sin\phi$; $e^{-i\phi} = \cos\phi - i\sin\phi$; $e^{2i\phi} = \cos 2\phi + i\sin 2\phi$ and $e^{-2i\phi} = \cos 2\phi - i\sin 2\phi$
4. The s orbitals consist only of a radial part to the wave function, and $Y = 1$.
5. The angular wave functions for other types of orbitals are complicated mathematical expressions, so generally only the shapes of the orbitals are important.

2.4.6 Radial functions R(r)

The radial function $R(r)$ describes how the electron density changes with distance from the nucleus. Plots of $R(r)$ against r (or ψ vs r) for selected orbitals are given below:

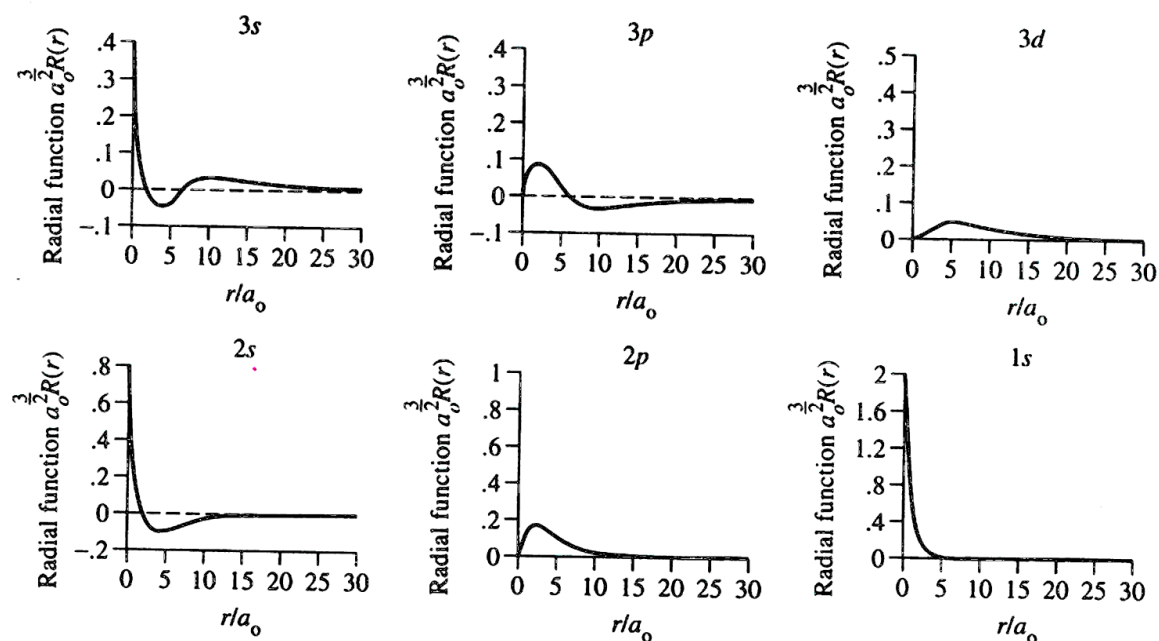


Figure 4: Plot of Radial Wave function (in atomic units) versus distance r (in atomic units) from the nucleus (diagram from Miessler & Tarr).

Notes

1. The point at which the radial wave function $R(r) = 0$ (except the origin) is called a radial node.
2. The sign of the radial wave function $R(r)$ changes (from +ve to -ve or vice versa) after passing the radial node
3. The number of radial nodes for a given orbital is given by $n-(l+1)$. For example,
 - a) ns orbitals have $(n-1)$ radial nodes, e.g. $2s$ has 1 radial node.
 - b) np orbitals have $(n-2)$ radial nodes, e.g. $2p$ has 0 radial node, $3p$ has 1 radial node.
 - c) nd orbitals have $(n-3)$ radial nodes, e.g. $3d$ has 0 radial node, $5d$ has 2 radial nodes.
 - d) nf orbitals have $(n-4)$ radial nodes, e.g. $4f$ has 0 radial node.
 - e) $1s$ orbital has no radial node.
 - f) $2s$ orbital has two regions of maximum probability, separated by a spherical surface of zero probability (1 radial node)
 - g) $3s$ orbital has three regions of maximum probability, separated by two radial nodes.

2.4.7 Radial distribution function $4\pi r^2 R(r)$

The radial distribution function is a probability function that tells us where an electron will most likely be found at a given distance from the nucleus. Plots of radial distribution

functions for 1s, 2s and 3s orbitals show that there is at least one maximum and the fact that an electron tends to be further from the nucleus as its principal quantum number n increases. *Therefore the size of an atomic orbital increases as the principal quantum number n increases.*

The radial distribution function is related to the radial wave function by the following relationship:

$$p_{n,l}(r) = 4\pi r^2 R_{n,l}(r); \text{normalized by } \int_0^\infty P_{nl}(r) dr = 1$$

The factor $4\pi r^2$ arises because the *radial distribution function* refers to the probability of finding an electron not at a specific point in space (which equals ψ^2), but on a spherical shell of area $4\pi r^2$, at a distance r from the nucleus. The integral results from the fact that the total probability of finding the electron is one, as it must be found somewhere around the nucleus.

Plots of radial distribution functions for 3s, 3p and 3d orbitals show that s orbital has electron density closest to the nucleus than p and d orbitals. We say that an electron in an s orbital is more penetrating than that in a p or d orbital.

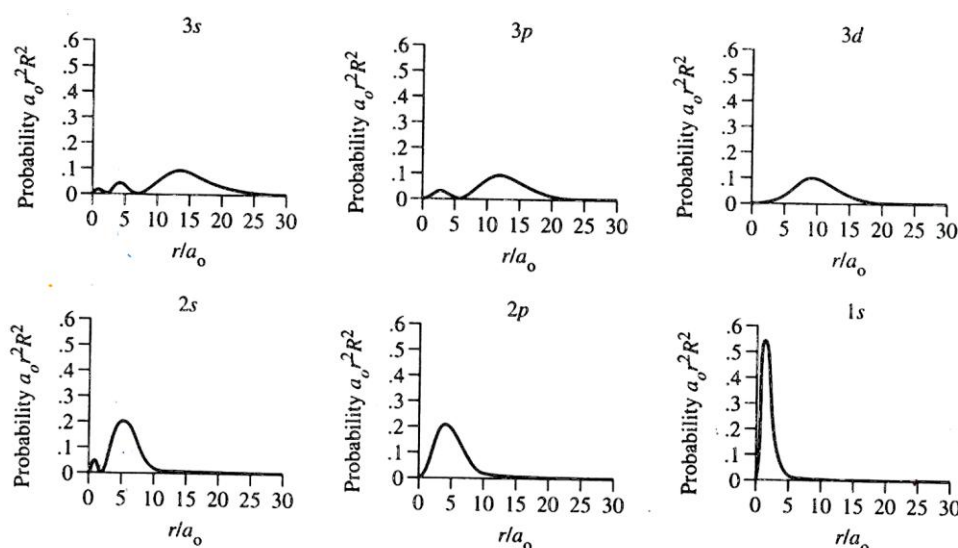


Figure 5: Plot of radial distribution function $4\pi r^2 R(r)$ for 1s, 2s, 2p, 3s, 3p, 3d orbitals of the hydrogen atom (diagram from Miessler & Tarr).

In all the plots, the electron density, or the probability of finding the electron, falls off rapidly as the distance from the nucleus increases. All the orbitals have zero probability at the centre of the nucleus because $4\pi r^2 R^2 = 0$ at $r = 0$.

2.4.8 Pictorial representation of atomic orbitals

The angular function $\Theta(\theta)$ and $\Phi(\phi)$ determine how the probability changes from point to point at a given distance from the centre of the atom. In actual fact they give the shape of the orbitals and their orientation in space. The angular functions $\Theta(\theta)$ and $\Phi(\phi)$ are determined by the quantum numbers l and m_l .

When the $\Theta(\theta)$ portion of the angular function is plotted the shape the function can be obtained. When the $\Phi(\phi)$ is included, with values of $\phi = 0$ to 2π , the three dimensional shapes/surfaces are formed. Thus an atomic orbital is defined as a boundary surface which encloses 95 % of the electron density for a particular wave function, ψ . They can be represented pictorially by boundary surface diagrams or electron density contour plots.

s orbitals

For these orbitals, $l = 0$, $m_l = 0$, the angular wave function $Y(\theta, \phi)$ is independent of the angles θ and ϕ . Therefore, an s orbital is spherically symmetrical about the nucleus.

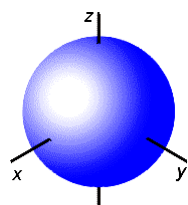


Figure 6: Boundary surface diagram of an s orbital. (Figure taken from Shriver & Atkins)

p orbitals

For these orbitals, $l = 1$; $m_l = -1, 0, +1$ and there are 3 possible orientations of p orbitals: along the x, y and z axes. They are dumb-bell shaped i.e. the electron density is concentrated in two identical lobes on either side of the nucleus.

The p_z orbital has an angular node (point where $Y(\theta, \phi) = 0$) along the xy plane; p_x orbital has an angular node along the yz plane; p_y orbital has an angular node along the xz plane.

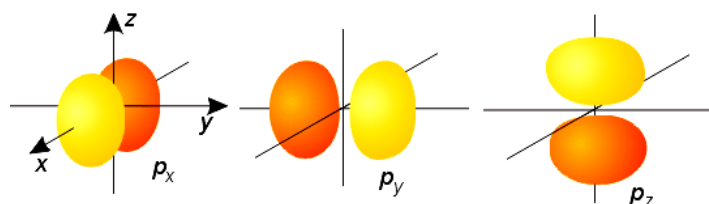


Figure 7: Boundary surface diagram of p orbitals. The lightly shaded lobe has a positive amplitude; the more darkly shaded lobe is negative (Figure taken from Shriver & Atkins)

Note the colour coding of the lobes and the nodes. The deep orange colour shows the negative phase of the function while the brighter one (yellow) is where the function has a positive phase.

d orbitals

In these orbitals, $l = 2$, $m_l = -2, -1, 0, +1, +2$. There are five d orbitals: d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and d_{z^2} . They have clover leaf shapes and have 4 lobes of maximum electron probability centered in the plane indicated in the orbital label. The four lobes are separated by two nodal planes through the nucleus.

d_{xy} , and $d_{x^2-y^2}$ are both centered in the xy plane but while the lobes of d_{xy} lie between the axes those of $d_{x^2-y^2}$ lie directly on the axes. The d_{yz} , d_{xz} orbitals have their lobes in between the respective axes. d_z^2 has two lobes along the z axis and a "belt" centered in the xy plane.

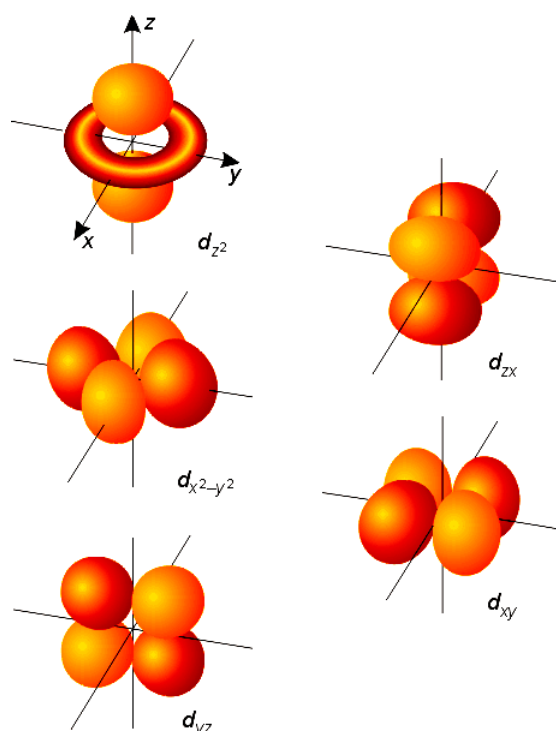


Figure 8: Boundary surface diagram of d orbitals. The lightly shaded lobe has a positive amplitude; the more darkly shaded lobe is negative (Figure taken from Shriver & Atkins).

2.5 Electronic Configurations

Here we attempt to answer the following questions:

- 1 What determines the orbitals in which electrons reside?
- 2 How do the electrons in a many-electron atom populate the available orbitals?

2.5.1 Energy Levels in Hydrogen and Other Atoms

For H, the energy of the electron only depends on n , principal quantum number. For a given n the s , p , d , f orbitals have the same energy. In the ground state, the electron in the H atom resides on the $1s$ orbital. For other atoms with more than one electron, electron-electron repulsion and shielding play a role so **energy depends on angular momentum quantum number l as well as the principal quantum number n** . The energies of the atomic orbitals in multi-electron atoms are arranged in the order, $ns < np < nd < nf$. This ordering can be explained by considering the possibility of having electron density closest to the positively charged nucleus in different atomic orbitals. The plot of radial distribution functions, $4\pi r^2 R(r)^2$, for $3s$, $3p$, $3d$ orbitals versus radius (r) (Fig. 5) shows the first maximum for the s orbital is closest to the nucleus than the p or d orbitals, i.e., the s orbital has electron density closest to the nucleus. We say that electrons in an s orbital can penetrate closer to the nucleus than an electron in a p , d , or f orbital can. Since orbitals with electron density closer to the

nucleus are more stable, therefore, for a given n , the energy of the orbital increases in the order: $s < p < d < f$.

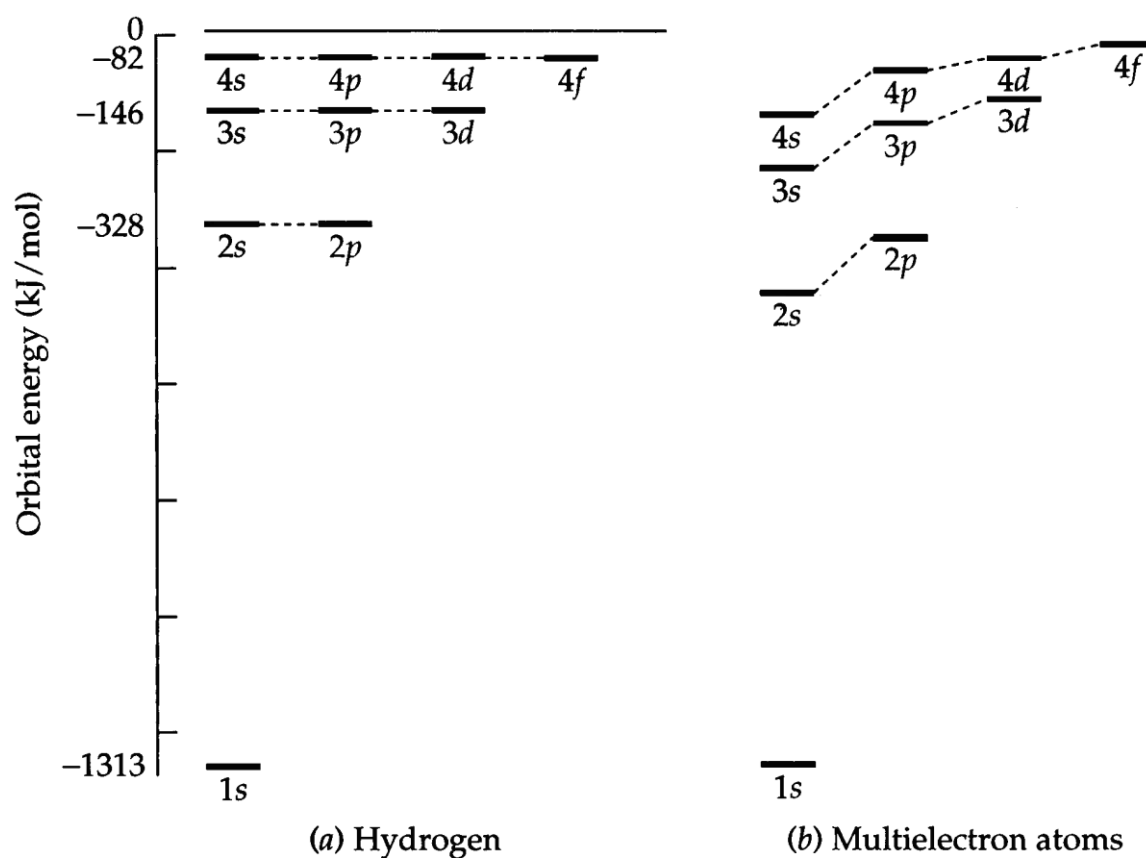


Figure 9: Orbital energy level diagrams for a hydrogen atom and multi-electron atoms (diagram taken from McMurry & Fay)

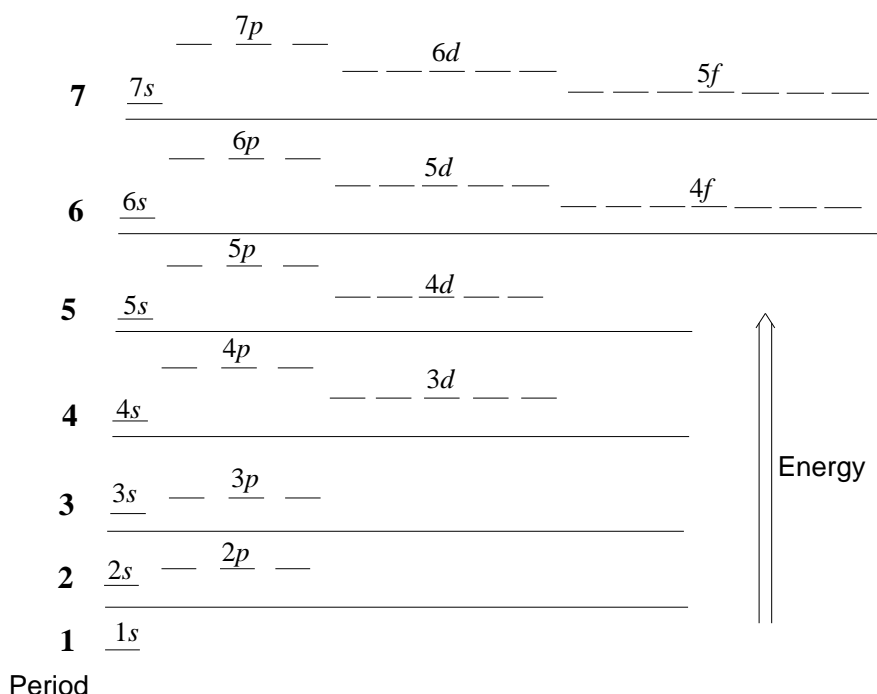


Figure 10: Relative energy level of various atomic orbitals in a multi-electron atom (diagram from Rayner-Canham).

Note that for $n > 2$ values in the energies of ns and $(n - 1) d$ orbitals, there are crossover points (e.g., $4s < 3d$; $5s < 4d$; $6s < 5d$; $7s < 6d$), this becomes important when filling electrons in multi-electron atoms. The effect is so pronounced for d and f electrons that they lie at higher energy than the s or p of the $(n + 1)$ shell in some cases. For example, energies of $3d > 4s$, $4d > 5s$; $4f > 5s$, $5p$.

2.5.2 Electronic Configurations

These describe how electrons are distributed in various orbitals in an atom. The filling of orbitals with electrons is governed by the following principles:

i). *The Aufbau Principle (Building up)*

Lowest energy orbitals are filled with electrons first. These correspond to the lowest values of n and l .

ii). *The Pauli Exclusion Principle*

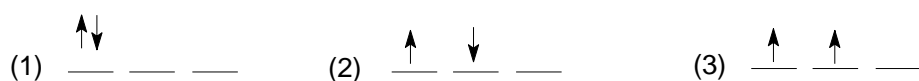
No two electrons in an atom can have the same four quantum numbers. Thus each electron is required to have a unique set of quantum numbers i.e. at least one quantum numbers must be different from those of every other electron. The effect of this is that only two electrons with opposite spins can occupy an orbital.

iii). *Hund's rule of maximum multiplicity*

This requires that electrons be placed in orbitals so as to give the maximum total spin possible (or the maximum number of parallel spins or unpaired electron). Two electrons in the same orbital have a higher energy than two electrons in different orbitals (due to electrostatic repulsion). Multiplicity is the number of unpaired electrons plus 1 or $n + 1$. It is the number of possible energy levels that depend on the orientation of the net magnetic moment in a magnetic field. Thus, if two or more degenerate orbitals (i.e. orbitals with the same energy) are available, electrons go into each degenerate orbital with parallel spins until the orbitals are half-filled.

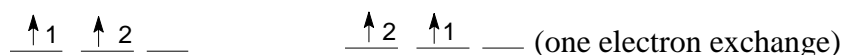
This rule is a consequence of the energy required for pairing electrons in the same orbital. Two electrons occupying the same space around an atom repel each other with a Coulombic energy of repulsion, Π_c , per pair of electrons. In addition there is exchange energy Π_e which arises from purely quantum mechanical considerations. The exchange energy depends on the number of possible exchanges between two electrons with the same energy and the same spin.

For example, the electron configuration of a carbon atom is $1s^2 2s^2 2p^2$. Three arrangements are considered for the electrons in the p orbitals:



Arrangement 1 involves Coulombic energy, Π_c , since it pairs electrons in the same orbital. The energy of this arrangement is higher than that of the other two by Π_c due to electron-electron repulsion.

In cases 1 and 2 there is only possible way to arrange the electrons to give the same diagram because there is only a single electron in each having + or – spin. On the other hand in case 3 there are two possible ways of exchanging the electrons without it being noticed (arranging the electrons to give the same diagram):



The exchange energy is Π_e per possible exchange of parallel electrons and is negative. The higher the number of possible exchanges the lower the energy. Thus, in this case the third configuration is of lower energy (more stable) than the second by Π_e .

When the orbitals are degenerate both Coulombic and pairing energies favour the unpaired configuration over the paired configuration. If there is a difference in energy between the levels, this difference in combination with the total pairing energy determines the final configuration. For atoms this means one set of orbitals gets filled before another has any electrons. However this breaks down in some of the transition elements, because the 4s and 3d (or the higher corresponding levels) are so close in energy that the pairing energy is nearly the same as the difference between levels.

2.5.4 Order of orbital filling in many-electronic atoms

Many schemes have been used to predict the order of filling of atomic orbitals. **Klechkowsky's** rule states that the order of filling the orbitals proceeds from the lowest available value of the sum $n+l$. When two combinations have the same value, the one with

the smaller value of n is filled first. Combined with the other rules, this gives the order of filling of most of the orbitals. It turns out then the order is generally as follows:

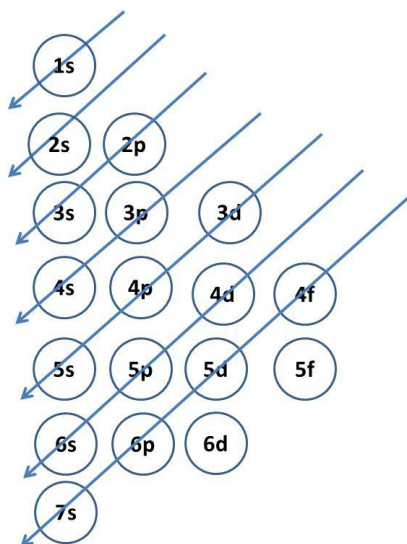


Figure 11: Order of orbital filling in many-electronic atoms

2.5.5 Shielding/Screening

In atoms with more than one electrons, energies of specific levels are difficult to predict quantitatively, but one of the commonest approaches is to use the idea of shielding. Each electron acts as a shield for electrons further out from the nucleus, reducing the attraction between the nucleus and the distant electrons.

Although the principal quantum number n is the most important in determining the energy, l must also be included in the calculation of the energy in atoms with more than one electron. As the atomic number increases (Z), the electrons are drawn toward the nucleus and the orbital energies become more negative (orbitals become more stable), but the changes are irregular because of the shielding of the outer electron by inner electrons. The resulting order of filling is given in Table 2.3.

The shielding of outer electrons by inner orbitals means that the outer electrons do not experience the expected nuclear charge. Instead, the outer electrons experience a reduced nuclear charge known as the effective nuclear charge Z^* . Slater formulated a set of simple rules that serve as a rough guide to this effect.

According to Slater, Effective nuclear charge, $Z^* = Z - S$, where Z is the nuclear charge and S is the screening constant. The rules for determining S for a specific electron are as follows:

- i) Write out the electron configuration of an atom in groupings as follows: $(1s)$, $(2s, 2p)$, $(3s, 3p)$, $(3d)$, $(4s, 4p)$, $(4d)$, $(4f)$, $(5s, 5p)$ etc.
- ii) Electrons with higher n (Those to the right in the list above) do not shield those in lower groups.
- iii) For ns or np valence electrons:
 - Electrons in the same ns , np group contribute, $S = 0.35$, except the $1s$ where 0.30 works better.
 - Each electrons in the $(n - 1)$ shell, contribute $S = 0.85$.
 - Each electrons in the $(n - 2)$ or lower shell, contribute $S = 1.00$
- iv) If the electron in question resides in a nd or nf orbitals, then,
 - Each of the other electron in the same nd , nf group, $S = 0.35$.
 - Electrons in the groups to the left i.e. $(n - 1)etc$ shell, contribute $S = 1.00$

The shielding constant S obtained from the sum of the contributions above is subtracted from the nuclear charge Z to obtain the effective nuclear charge Z^* affecting the selected electron.

Table 3: Filling of electrons for the first 30 elements

Atom	Atomic number	Electronic configuration	Atom	Atomic number	Electronic configuration
H	1	$1s^1$	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
He	2	$1s^2$	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Li	3	$1s^2 2s^1$	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Be	4	$1s^2 2s^2$	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
B	5	$1s^2 2s^2 2p^1$	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
C	6	$1s^2 2s^2 2p^2$	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
N	7	$1s^2 2s^2 2p^3$	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
O	8	$1s^2 2s^2 2p^4$	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
F	9	$1s^2 2s^2 2p^5$	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
He	10	$1s^2 2s^2 2p^6$	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Na	11	$1s^2 2s^2 2p^6 3s^1$	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Mg	12	$1s^2 2s^2 2p^6 3s^2$	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Example

1. Calculate the effective nuclear charge for the outermost electron in Oxygen, given the electron configuration of O is $1s^2 2s^2 2p^4$.

The electrons are grouped as follows: $(1s^2) (2s^2, 2p^4)$

$$\begin{aligned}
 Z^* &= Z - S \\
 &= 8 - [2 \times (0.85)] - [5 \times (0.35)] = 4.55 \\
 &\quad (1s) \quad \quad (2s, 2p)
 \end{aligned}$$

The two $1s$ electrons contribute 0.85 and the five $2s$ and $2p$ (We are finding Z^* for the sixth electron and so it's not counted) each contribute 0.35 for a total shielding constant $S = 3.45$. Thus the net effective nuclear charge $Z^* = 4.55$. This implies that the last electron is held with about 57% of the force expected for a +8 nucleus and a -1 electron.

2. Calculate the effective nuclear charge on a 3d electron in a Nickel atom.

The electron configuration of Ni: $(1s^2) (2s^2, 2p^6) (3s^2, 3p^6) (3d^8) (4s^2)$.

$$\begin{aligned}
 &\text{For a 3d electron,} \\
 Z^* &= Z - S \\
 &= 28 - [18 \times (1.00)] - [7 \times (0.35)] = 7.55
 \end{aligned}$$

The 18 electrons in the $1s$, $2s$, $2p$, $3s$, and $3p$ levels contribute 1.00 each, the other 7 in $3d$ contribute 0.35. The $4s$ contribute nothing.

Self-assessment Exercise

Calculate the effective nuclear charge on a 4s electron in a Nickel atom, given the electron configuration of Ni: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

2.6 The Periodic Table

Elements are arranged with increasing atomic number in rows (called periods) and columns (called groups).

- Elements in Groups 1 and 2 are also called *s* block elements: valence electrons fill in *s* orbitals.
- Elements in Groups 13 to 18 are also called *p*-block elements: valence electrons fill in *p* orbitals.
- Elements in Groups 1, 2 and 13 - 18 are called main group elements.
- Elements in Groups 3 - 12 are called transition metal because they have partially filled *d*-orbitals. They are also called *d*-block elements because valence electrons are contained in *d* orbitals.
- *f*-block elements (also called Lanthanides and Actinides) have valence electrons filling in *f* orbitals.
- Elements in each group have similar valence electron configuration (electrons in the outermost shell) and therefore similar properties.

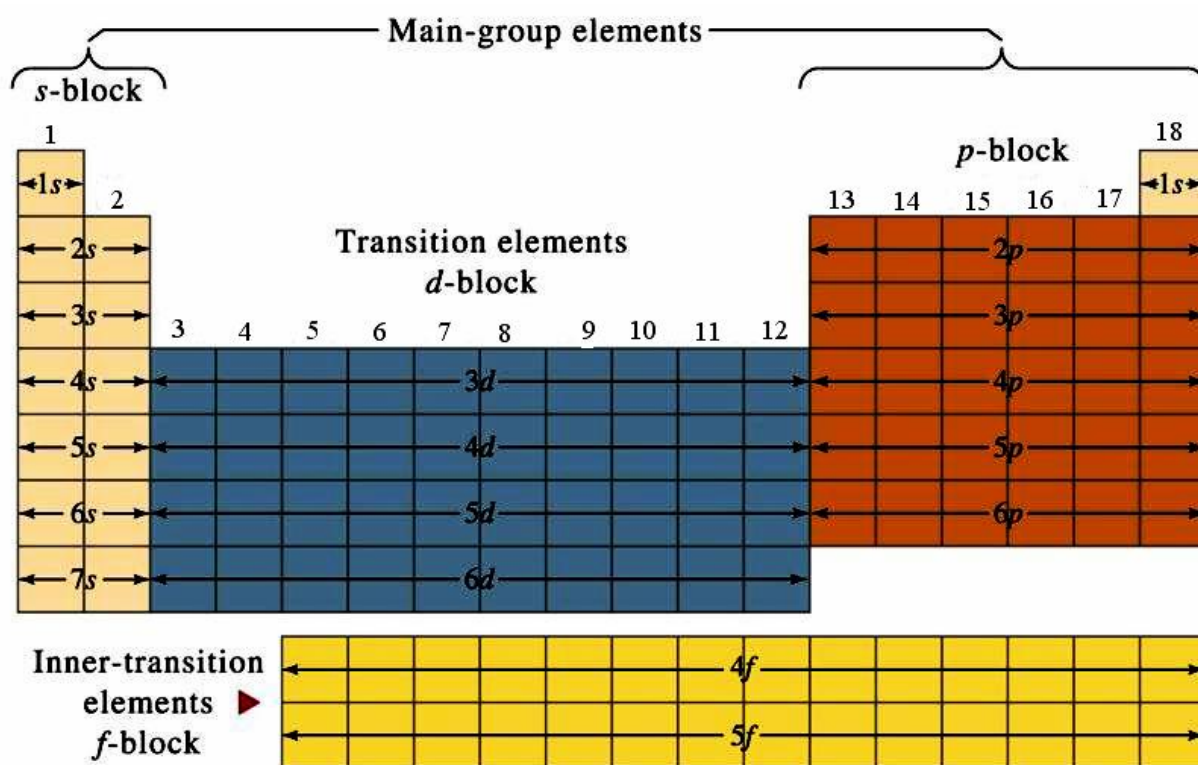


Figure 12: Sections of the Periodic Table (http://en.wikipedia.org/wiki/Periodic_table)

Periodic Table of the Elements
and ground-state electronic configurations
(see opposite for Table of Standard Atomic Weights)

Period ↓	<table><tr><td>1</td><td>2</td></tr><tr><td>H 1s¹</td><td>He 1s²</td></tr></table>																		1	2	H 1s ¹	He 1s ²																		
	1	2																																						
H 1s ¹	He 1s ²																																							
1	1	2											13	14	15	16	17	18																						
2	3 Li [He]2s ¹	4 Be [He]2s ²											5 B 2s ² 2p ¹	6 C 2s ² 2p ²	7 N 2s ² 2p ³	8 O 2s ² 2p ⁴	9 F 2s ² 2p ⁵	10 Ne 2s ² 2p ⁶																						
3	11 Na [Ne]3s ¹	12 Mg [Ne]3s ²	3	4	5	6	7	8	9	10	11	12	13 Al 3s ² 3p ¹	14 Si 3s ² 3p ²	15 P 3s ² 3p ³	16 S 3s ² 3p ⁴	17 Cl 3s ² 3p ⁵	18 Ar 3s ² 3p ⁶																						
4	19 K [Ar]4s ¹	20 Ca [Ar]4s ²	21 Sc 3d ¹ 4s ²	22 Ti 3d ² 4s ²	23 V 3d ³ 4s ²	24 Cr 3d ⁵ 4s ¹	25 Mn 3d ⁵ 4s ²	26 Fe 3d ⁶ 4s ²	27 Co 3d ⁷ 4s ²	28 Ni 3d ⁸ 4s ²	29 Cu 3d ¹⁰ 4s ¹	30 Zn 3d ¹⁰ 4s ²	31 Ga 4s ² 4p ¹	32 Ge 4s ² 4p ²	33 As 4s ² 4p ³	34 Se 4s ² 4p ⁴	35 Br 4s ² 4p ⁵	36 Kr 4s ² 4p ⁶																						
5	37 Rb [Kr]5s ¹	38 Sr [Kr]5s ²	39 Y 4d ¹ 5s ²	40 Zr 4d ² 5s ²	41 Nb 4d ⁴ 5s ¹	42 Mo 4d ⁵ 5s ¹	43 Tc 4d ⁵ 5s ²	44 Ru 4d ⁷ 5s ¹	45 Rh 4d ⁸ 5s ¹	46 Pd 4d ¹⁰	47 Ag 4d ¹⁰ 5s ¹	48 Cd 4d ¹⁰ 5s ²	49 In 5s ² 5p ¹	50 Sn 5s ² 5p ²	51 Sb 5s ² 5p ³	52 Te 5s ² 5p ⁴	53 I 5s ² 5p ⁵	54 Xe 5s ² 5p ⁶																						
6	55 Cs [Xe]6s ¹	56 Ba [Xe]6s ²	57 La 5d ¹ 6s ²	72 Hf 5d ² 6s ²	73 Ta 5d ³ 6s ²	74 W 5d ⁴ 6s ²	75 Re 5d ⁵ 6s ²	76 Os 5d ⁶ 6s ²	77 Ir 5d ⁷ 6s ²	78 Pt 5d ⁹ 6s ¹	79 Au 5d ¹⁰ 6s ¹	80 Hg 5d ¹⁰ 6s ²	81 Tl 6s ² 6p ¹	82 Pb 6s ² 6p ²	83 Bi 6s ² 6p ³	84 Po 6s ² 6p ⁴	85 At 6s ² 6p ⁵	86 Rn 6s ² 6p ⁶																						
7	87 Fr [Rn]7s ¹	88 Ra [Rn]7s ²	89 Ac 6d ¹ 7s ²	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub																												
* 58 Ce 4f ¹ 5d ¹ 6s ²																					59 Pr 4f ³ 6s ²	60 Nd 4f ⁴ 6s ²	61 Pm 4f ⁵ 6s ²	62 Sm 4f ⁶ 6s ²	63 Eu 4f ⁷ 6s ²	64 Gd 4f ⁷ 5d ¹ 6s ²	65 Tb 4f ⁹ 6s ²	66 Dy 4f ¹⁰ 6s ²	67 Ho 4f ¹¹ 6s ²	68 Er 4f ¹² 6s ²	69 Tm 4f ¹³ 6s ²	70 Yb 4f ¹⁴ 6s ²	71 Lu 4f ¹⁴ 5d ¹ 6s ²							
† 90 Th 6d ² 7s ²																					91 Pa 5f ² 6d ¹ 7s ²	92 U 5f ³ 6d ¹ 7s ²	93 Np 5f ⁴ 6d ¹ 7s ²	94 Pu 5f ⁶ 7s ²	95 Am 5f ⁷ 7s ²	96 Cm 5f ⁷ 6d ¹ 7s ²	97 Bk 5f ⁹ 6d ¹ 7s ²	98 Cf 5f ¹⁰ 7s ²	99 Es 5f ¹¹ 7s ²	100 Fm 5f ¹² 7s ²	101 Md 5f ¹³ 7s ²	102 No 5f ¹⁴ 7s ²	103 Lr 5f ¹⁴ 6d ¹ 7s ²							

*†The ground-state configurations for some lanthanide and actinide elements are uncertain

Figure 2.13: The standard periodic Table (From: http://en.wikipedia.org/wiki/Periodic_table, slightly modified)

2.6.1 Periodic Trends of Atomic Parameters

Atomic properties such as effective nuclear charge, atomic radii, ionization energies, electron affinity and electronegativity are important in accounting for the chemical properties of an element.

2.6.2 Periodic Trend in Effective Nuclear Charge

Below is a table of the values of effective nuclear charge (Z_{eff}) for s and p electrons in elements Li - Ne:

Element	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76

- In the same atom, each electron with different n and l values can have a different Z_{eff} because the repulsive effects due to the other electrons is different. E.g., the Z_{eff} for the B atom: $1s \gg 2s > 2p$ and the size of orbitals is: $1s \ll 2s < 2p$
- For the same n and l value, Z_{eff} increase across a period (e.g., from Li to Ne) as Z increases. As a result, the size of the orbital decreases (electrons gets closer to the nucleus) and the size of the atoms decreases. E.g. the Z_{eff} for the $2p$ orbitals: $B < C < N < O < F < Ne$ and the size of the $2p$ orbitals is: $B > C > N > O > F > Ne$

2.6.3 Sizes of Atoms and Ions

- Since electrons can only be located by probability, there is no real boundary to an atom.
- Radii of atoms and ions are obtained experimentally from measuring bond lengths in molecules, metals and ionic crystals by X-ray diffraction.

Covalent radii r_{cov}

- Defined as half the distance between the nuclei of two atoms of the same element joined by a covalent bond. E.g., Cl_2 bond distance = 198 pm, atomic radius of Cl = $(198)/2 = 99$ pm.

Van der Waals radius r_{vdw}

- Defined as half the distance between the nuclei of two non-bonded atoms or molecules.
- Obtained from the closest approach between two non-bonded atoms or molecules in the solid state. E.g., van der Waals radius of Cl = 180 pm.
- In general, $r_{\text{vdw}} > r_{\text{cov}}$.

Ionic radius

- Defined as the distance between the nuclei of adjacent cations and anions in a purely ionic lattice.

In general, $r_{\text{anions}} > r_{\text{cov}} > r_{\text{cation}}$ for any given element.

For example ionic radius of sodium ion, $r_{\text{Na}^+} = 116 \text{ pm}$ while covalent radius of sodium atom, $r_{\text{Na}} = 154 \text{ pm}$.

Explanation of the difference

From Na ($1s^2 2s^2 2p^6 3s^1$) to Na^+ ($1s^2 2s^2 2p^6$) Z_{eff} increases since the number of electrons decreases.

The covalent radius of chlorine, $r_{\text{Cl}} = 97 \text{ pm}$ while the ionic radius of the chloride ion $r_{\text{Cl}^-} = 167 \text{ pm}$;

Explanation of the difference

From $\text{Cl}(1s^2 2s^2 2p^6 3s^2 3p^5)$ to $\text{Cl}^- (1s^2 2s^2 2p^6 3s^2 3p^6)$: Z_{eff} decreases since no. of electrons increases.

2.6.4 Periodic Trends in Atomic Radii

- Across a row**, the atomic radius decreases because the n value for the outer shell remains the same but Z_{eff} is increasing.
 - E.g. For the row started by Na the outer shell is $3s^1, 3s^2, 3s^2 3p^1, 3s^2 3p^2, \dots, 3s^2 3p^6$. The atomic radius decreases (from Na to Ar) because the Z value is increasing and the added electrons do not completely shield the outer electrons from the increased Z .
- Down a group**, the increase in Z_{eff} does not completely counteract the fact that the outer electrons are in orbitals with higher n , so radius increase down a group. There is an increase in the number of occupied orbitals.
 - E.g. For group headed by Be outer shell is $2s^2, 3s^2, 4s^2, 5s^2, 6s^2, 7s^2$, atomic size increases from Be to Ra.

Table 4: Covalent radii (pm) of some selected elements

Li	Be	B	C	N	O
132	89	82	77	77	73
Na	Mg	Al	Si	P	S
154	136	118	111	106	102
K	Ca	Ga	Ge	As	Se
203	174	126	122	120	117
Rb	Sr	In	Sn	Sb	Te
216	191	144	140	140	136

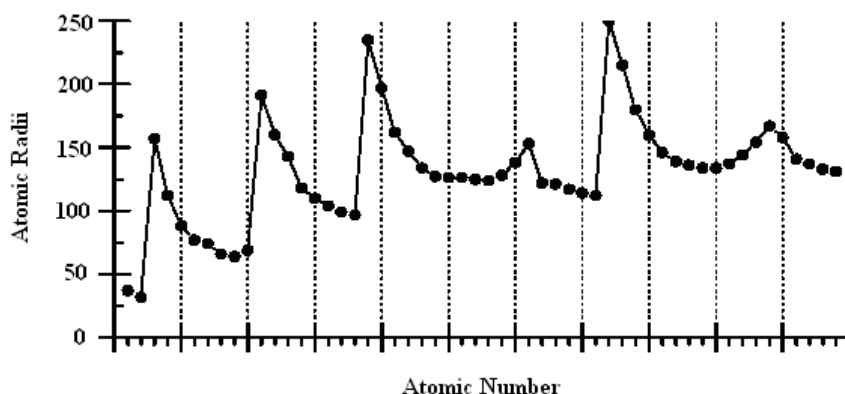


Figure 13: Variation of atomic radii with atomic number (across the periods)

2.6.5 Periodic Trends in Ionic Radii

Down a group in cations and anions- sizes increase, e.g.

- $\text{Mg}^{2+}(2s^22p^6) > \text{Ca}^{2+}(3s^23p^6) > \text{Sr}^{2+}(4s^24p^6) > \text{Ba}^{2+}(5s^25p^6)$
- $\text{F}^-(2s^22p^6) > \text{Cl}^-(3s^23p^6) > \text{Br}^-(4s^24p^6) > \text{I}^-(5s^25p^6)$
- n value of outer orbital increase but is not counteracted by the increasing Z_{eff} .

Size of isoelectronic series (ions/atoms containing the same number of electrons):

- $\text{O}^{2-}(2s^22p^6) > \text{F}^-(2s^22p^6) > \text{Ne}(2s^22p^6) > \text{Na}^+(2s^22p^6) > \text{Mg}^{2+}(2s^22p^6)$
- Z_{eff} increasing > Since same no. of electrons and Z increasing.
- $r(\text{O}^{2-}) > r(\text{F}^-) > r(\text{Ne}) > r(\text{Na}^+) > r(\text{Mg}^{2+})$

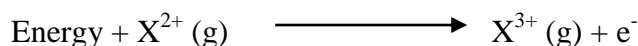
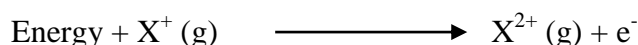
Table 5: Ionic radii (pm) of some selected main group ions

Li⁺	Be²⁺		O²⁻	F⁻
60	31		140	136
Na⁺	Mg²⁺	Al³⁺	S²⁻	Cl⁻
95	65	50	184	181
K⁺	Ca²⁺	Ga³⁺	Se²⁻	Br⁻
133	99	62	198	
Rb⁺	Sr²⁺	In³⁺	Te²⁻	I⁻
248	113	81	221	216

2.6.6 Periodic Trends in the First Ionization Energy

The ionization energy of an atom is the minimum energy required to remove an electron from a gaseous atom in its ground state. The magnitude of ionization energy is a measure of the effort required to force an atom to give up an electron, the higher the ionization energy, the more difficult it is to remove the electron.

For many-electron atom, the amount of energy required to remove the first electron from the atom in its ground state is called the **first ionization energy (I_1)**. The second ionization energy (I_2) and the third ionization energy (I_3) are shown in the following equations:



Higher ionization potentials labeled I^2 , I^3 , I^4 and so on will correspond to the successive removal of additional electrons. The table below gives the first ionization energies of the first 20 elements.

Table 6: Ionization Potential (Energy) for the First 20 Elements

Element	1st	2nd	3rd	4th	5th	6th	Element	1st	2nd	3rd	4th	5th	6th
¹ H	1312						¹¹ Na	495.9	4560	6900	9540	23400	16600
² He	2373	5248					¹² Mg	738.1	1450	7730	10500	13600	18000
³ Li	520	7300	11808				¹³ Al	577.9	1820	2750	11600	14800	18400
⁴ Be	899	1757	14850	20992			¹⁴ Si	786.3	1580	3230	4360	16000	20000
⁵ B	801	2430	3660	25000	32800		¹⁵ P	1012	1904	2910	4960	6240	21000
⁶ C	1086	2350	4620	6220	38000	47232	¹⁶ S	999.5	2250	3360	3660	6990	8500
⁷ N	1400	2860	4580	7500	9400	53000	¹⁷ Cl	1251	2297	3820	5160	6540	9300
⁸ O	1314	3390	5300	7470	11000	13000	¹⁸ Ar	1521	2666	3900	5770	7240	8800
⁹ F	1680	3370	6050	8400	11000	15200	¹⁹ K	418.7	3052	4410	5900	8000	9600
¹⁰ Ne	2080	3950	6120	9370	12200	15000	²⁰ Ca	589.5	1145	4900	6500	8100	11000

Ionization energies are positive quantities. If the ionization Energy was plotted against the atomic number, the periodicity will be clearly evident. The 1st Ionization energy generally increases across the period. Group I elements (alkali metals) have the lowest ionization energies. This is because the elements have one valence electron that is effectively shielded by the completely filled inner shells. Consequently, it is energetically easy to remove an electron from the atom of an alkali metal to form unipositive ion (Li^+ , Na^+ , K^+ ...).

On the other hand non-metals have much higher ionization energies. The ionization energies of the metalloids usually fall between those of metals and non-metals. This explains why metals readily form cations while non-metals form anions. However, there are irregularities in the increase of the ionization energy across the periods. For example going across the period from group 2 to 3, thus from Be to B and from Mg to Al. The group 3 elements have a single electron in the outermost sub level ($ns^2 np^1$), which is well shielded by the inner electrons and the ns^2 electrons. Less energy is therefore needed to remove a paired s electron from the same principle energy level. This brings about the lower ionization energies in group 3 elements compared with those in group 2 in the same period.

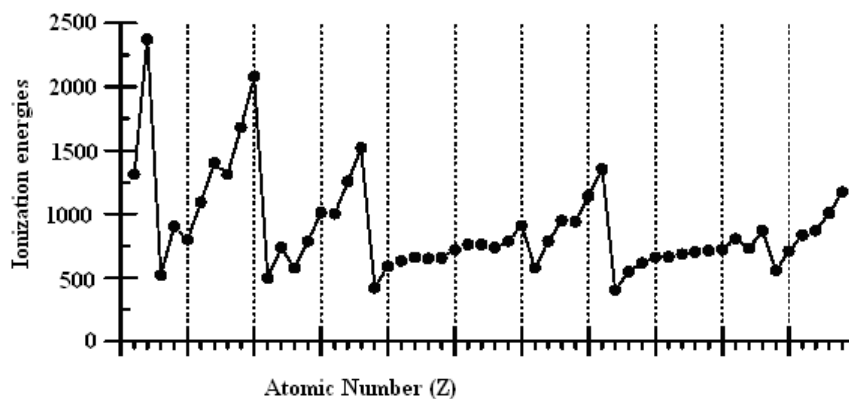


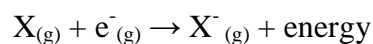
Figure 14: Ionization energies of the first 55 elements

The following observations are clear from the figure above:

- Ionization energy increases across each row, e.g. from Li to Ne; Na to Ar; K to Kr and so on (*because Z_{eff} increases and the electrons in a given orbital are held more tightly, therefore, to remove the electron from the atom requires more energy*).
- Group 1 (Alkali) metals (i.e. Li, Na, K, Rb, Cs and Fr) have minimum I.E. This is because they have only a single loosely held electron in the valence shell ns^1 .
- Group 18 (noble gases) (i.e. He, Ne, Ar, Kr, Xe and Rn) have the highest I.E. This is because they have a filled valence shell, ns^2np^6 and high effective nuclear charge, Z_{eff} . Thus valence electrons are tightly held.
- Minor irregularities can be seen; for example,
 - E.g. I.E. of Be = 899.4 kJ/mol while I.E. of B = 800.6 kJ/mol: *This can be attributed to there being a completely filled ns^2 configuration ($2s^2$) in Be while in B the arrangement is $2s^22p^1$ in B. The unpaired electron in B is easily lost leading to lower I.E.*
 - I.E of N = 1402.3 kJ/mol while the I.E. of O = 1313.9 kJ/mol. *This attributed to the stability of the half-filled p orbital in N ($2s^22p^3$). In O the valence electron arrangement is $2s^22p^4$ in which one p electron is paired and hence easily lost to reduce electron-electron repulsion.*
- I.E decreases down a group, e.g. $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs} > \text{Fr}$. Similarly $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe} > \text{Rn}$. *Due to electrons filling in larger shell (larger n), further away from the nucleus. Therefore, valence electrons are well shielded from the nucleus by inner shell electrons and are loosely held.*
 - The ionization energy increases only slightly across a row in the transition series (including lanthanides and actinides series).

2.6.7 Periodic Trend in Electron Affinity

The electron affinity of an atom is defined as the energy change obtained when a neutral atom in the gaseous state captures an electron. Thus, the energy is released by the reaction represented below



It is the reverse of the 1st ionization potential and may be looked at as the ability of an atom to accept one or more electrons. The largest electron affinities are those of the halogens. This is

as expected since the addition of one electron yields the stable octet configuration of the 18th group elements-the noble gases.

We assign a negative value to the affinity when energy is released. The more negative the electron affinity, the greater the tendency of the atom to accept an electron. The tendency to accept electrons increases as we move from left to right across the periodic table. Thus Electron Affinity becomes more negative. The E.A of metals are generally more positive (or less negative) than those of non-metals. The values differ little within a group, but the halogens have the most negative E.A values, while the noble gases that have filled outer s and p sub shells have no tendency to accept electrons. The E.A of oxygen has a negative value, which means that the process $O_{(g)} + e^- \rightarrow O^-_{(g)}$ is favourable, while that of the O^- i.e. $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}$ is positive (780kJ/mol) meaning that this process is not favourable in the gas phase.

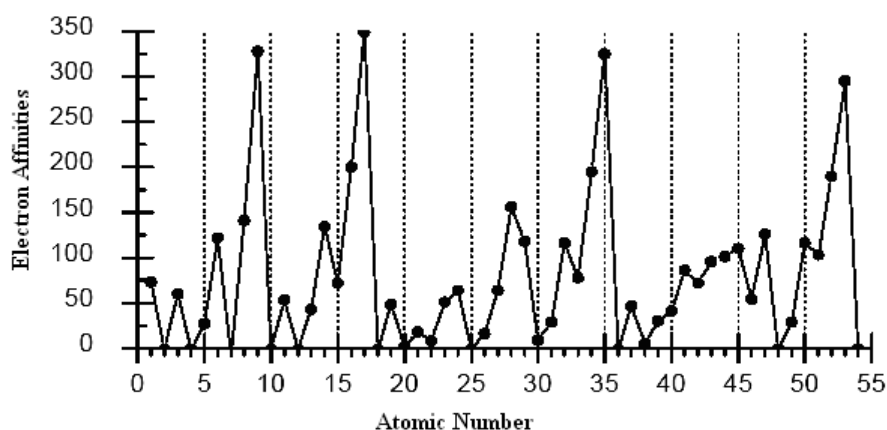


Figure 15: Variation of electron affinity with atomic number

2.6.8 Periodic Trends in Electronegativity, χ

The tendency of an atom to attract electrons to itself in a chemical bond is referred to as **electronegativity**. The greater the electronegativity of an atom, the more strongly the atom attracts the electrons of a bond. This concept was proposed by Linus Pauling in 1937. Electronegativity cannot be calculated accurately or measured directly. However, we expect it to depend on the magnitude of the charge and on the distance of the bonding pair of electrons from the nucleus. There are two important trends in electronegativity within the periodic table: -

- electronegativity increases across a period as the charge increases
- electronegativity generally decreases from top to bottom in a group; because with each successive shell, the bonding electrons are further from the nucleus.

Because the electronegativity of an atom cannot be defined quantitatively, it cannot be given a precise value but approximate values. Table shows the electronegativity values

Table 7: Electronegativity χ of some elements

Group → Period ↓	1	2	13	14	15	16	17	18
1	H 2.2							He -
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1	Ne -
3	Na 1.0	Mg 1.2	Al 1.3	Si 1.7	P 2.1	S 2.4	Cl 2.8	Ar -
4	K 0.9	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7	Kr 3.1
5	Rb 0.9	Sr 1.0	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2	Xe 2.4

Electronegativity may be used to estimate bond polarity. e.g.

- Atoms with similar electronegativity (i.e. $\Delta\chi \leq 0.4$) form non-polar bonds.
- Atoms whose electronegativity differs by more than 2 form ionic bonds.
- Atoms whose electronegativities differ by less than 2 form covalent bonds.

2.6.9 Common Oxidation States of the Elements

Oxidation number is the apparent charge assigned to an atom in a molecule or in a compound. Some oxidation numbers are fixed:

Elements	Oxidation number
O	-2 except in peroxide
H	+1 except in hydride
Group 1 metals	+1
Group 2 metals	+2
Halogens	-1 except in oxygen compounds